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COMPLETE SPECIFICATION.

Process for Directly Producing Glycerol-halogen-hydrins and Poly-oxy Fatty Acid Esters.

I, HENRY FAIRBROTHER, of 33, Cannon Street, London, Chartered Patent Agent, communication from:—Ernst Zollinger, of 57, Bellariastrasse, Zurich, Switzerland, Merchant, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

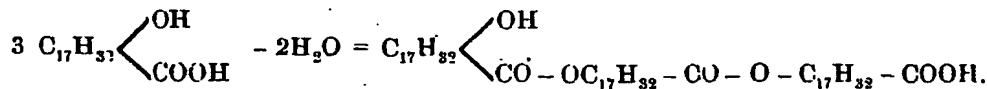
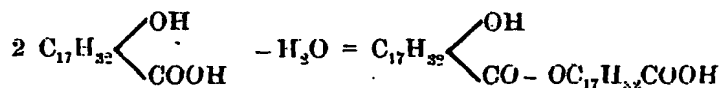
The glycerol chlorhydrins, that is to say the hydrochloric acid esters of glycerol have hitherto only been able to be prepared from free glycerol by the action of hydrochloric acid, hydrochloric acid gas, or chlorinating means, as for example sulphur chloride, thionyl-chloride and the like.

Now it has been discovered that halogenhydrins can be produced much more simply and practically in a single operation from fats containing the glycerol in chemical combinations, particularly easily from castor oil by allowing calculated quantities or excess of hydrochloric acid, with or without the presence of alcohol to act under pressure on the oil in question. The fat can be employed undiluted or in solution. There then occurs simultaneously or consecutively a plurality of chemical reactions, as for example in the case of the action of alcoholic hydrochloric acid on castor oil as follows:

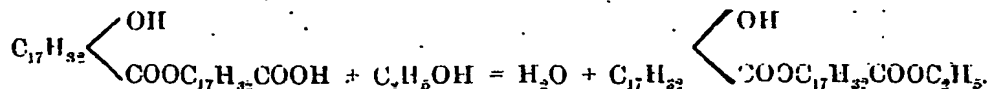
1. The triglyceride is split up by the hydrochloric acid into free ricinoleic acid and into ricinoleic acid esters of the chlorhydrin.

2. The chlorhydrin-ricinoleic acid esters are further split up into free chlorhydrin and ricinoleic acid.

3. The ricinoleic acid is condensed by the hygroscopic action of the hydrochloric acid and by splitting off 1 molecule of water from 2 molecules of ricinoleic acid forms the di-ricinoleic acid, and by splitting off 2 molecules of water from 3 molecules of ricinoleic acid forms the tri-ricinoleic acid according to the equations:



4. The poly-ricinoleic acids thus obtained are converted by the alcohol in the presence of the remaining excess of hydrochloric acid into their ethyl (and methyl) esters. For example



The main products of the reactions are glycerol mono-chlorhydrin, glycerol di-chlorhydrin and poly-ricinoleic acid esters, although the raw product also contains slight quantities of glycerol and free di- and tri-ricinoleic acid.

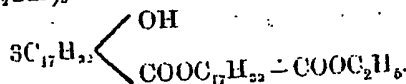
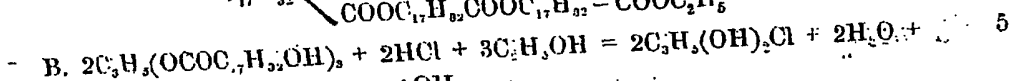
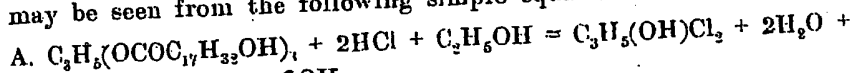
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The full course of the action of the hydrochloric acid and alcohol on castor oil cannot be easily shown in an equation, the formation of the important products may be seen from the following simple equations:



For carrying out the process all glycerides of fatty oxy-acids may be employed.

EXAMPLES:

I.

300 kg. of castor oil are diluted with 40—80 kg. of alcohol at 95% or with a corresponding quantity of methylated spirits, 30 kg. of hydrochloric acid gas 10 are introduced and the whole heated (say to 70°—80° Celsius) under pressure until on taking a sample it is seen that the reaction is terminated. The contents of the autoclave have separated into two layers, one a watery layer and the other an oily layer, each of which is heated separately in a vacuum. The watery solution will then yield 5—6 kg. mono-chlorhydrin (boiling point 15 138—140° at 18 mm.), from the oily layer there is first distilled 20—50 kg. alcohol, then 26—28 kg. glycerol di-chlorhydrin (boiling point about 80° C. at 18 mm.), and finally 5 kg. mono-chlorhydrin.

There will remain about 285 kg. poly-ricinoleic acid esters in the still. The yield of glycerol chlorhydrins amounts consequently to 90—98% of the 20 theoretical amount. The poly-ricinoleic acid esters are obtained quantitatively.

II.

100 kg. of oxydised linseed oil are mixed with 15—25 kg. of alcohol, such as methyl or ethyl and then 10 kg. of hydrochloric acid gas are introduced or a corresponding quantity of alcoholic hydrochloric acid is added to the oil. The 25 charge is heated (say to 70°—80° Celsius) whilst stirring in the autoclave until the calculated quantity of hydrochloric acid has been used up. The separation into the watery and oily layers as well as the isolating of the chlorhydrin is effected in exactly the same manner as in the Example I.

III.

32 kg. of hydrochloric acid gas are passed whilst cooling into 300 kg. of castor oil and the mass is then heated in an autoclave at about 10 atmospheres pressure for 12 to 18 hours at about 80° C. At the end of the reaction about 10 kg. of a liquid has separated out from the oil, which liquid consists of a solution of mono-chlorhydrin and some di-chlorhydrin and hydrochloric acid in the water 35 formed during the reaction. After separating the same from the oily layer the latter is distilled in a vacuum, whereby at a pressure of 20 mm. at 85° about 29 kg. of chlorhydrin pass over, that is about 70% of the theoretical quantity. Before distilling, the oily layer may be heated whilst stirring for another hour with alcohol, whereby there occurs a splitting up of the poly-ricinoleic acid 40 chlorhydrin esters contained in the raw product. On distilling there will then be obtained about 33 kg. of chlorhydrin, that is to say more than 80% of the theoretical quantity. The residues of the distillation do not differ from the poly-ricinoleic esters obtained in Example I. The watery portion of the reaction product is neutralised and subjected to fractional distillation, 45

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IV.

100 kg. of castor oil or the corresponding quantity of an oxydised oil, such as distilled linseed oil or oxydised train oil are mixed with a solution of 22 kg. of hydrobromic acid in the required or in an excess quantity of alcohol and the mass heated in the autoclave in accordance with the above-mentioned conditions until approximately the calculated quantity of hydrobromic acid has entered into combination.

At the end of the reaction both layers of the reaction product are separated and from each of them the bromhydrins are distilled off by heating under a vacuum up to 160—180° C. The yield amounts to 19½ kg., that is to say about 85% of the theoretical quantity. The poly-oxy-fatty ester is obtained quantitatively.

The products of condensation in the Examples 2—4 after distilling the halogen-hydrins remain as residues, just as the poly-ricinoleic acid esters when working according to Example I.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

Process for directly converting tri-glycerides (fats and oils) into glycerol-halogen-hydrins and condensation products of the fatty acids employed or in some cases esters of same, characterised in that the tri-glycerides are made to react undiluted or in solution with a calculated quantity or with an excess of halogen-hydrogen acids under pressure in the form of gas or dissolved in methyl or ethyl alcohol.

Dated this 26th day of June, 1913.

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